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A STUDY OF STARCHES
AT THE SIZE PRESS

By: Robert M. McDonald

A Thesis Submitted
to Dr. Stephen Kukolich
in Partial Fulfillment of
the Course Requirements for
the Bachelor of Science Degree

Western Michigan University
Kalamazoo, Michigan
April, 1980

ABSTRACT

A literature research is presented concerning the five different starches which were used. Also covered were size presses and how they affect paper properties. BOD was also covered, and how starch has a tremendous effect on it. The literature research indicates there are few quantitative results in this area.

The objective of the experimental work was to compare five different starches, applied at the size press, for physical and optical properties, and also BOD. The starches used were an ethylated, an oxidized, a cationic, a thermal-chemical and a thermal-chemical cationic. These five starches were applied at three solids levels and then tested.

Looking at the experimental results on an overall basis, the thermal-chemical cationic seemed to have come out on top on just about every test. Most impressive were the BOD results for the thermal-chemical cationic at 7 percent solids. It showed a considerable difference in BOD levels when compared to the other starches at the same consumption level.

ACKNOWLEDGEMENTS

I would like to take this opportunity to express my appreciation to the many people who helped make this study possible.

First of all, I would like to thank Dr. Stephen Kukolich, my advisor, for his interest, helpful suggestions, and most of all for his devoted confidence in me, which helped me to try and do my best.

I would also like to thank Grain Processing Corporation for the materials and help they gave me. My thanks also goes to Richard Harvey for his interest, continued support throughout the entire thesis, and also for the invaluable information I received from him.

A special thanks goes out to Fletcher Paper Company, which has been very supportive of me throughout my entire college career. Without their donation of materials and help, my thesis would never have happened.

To all, again,

Thank you very much

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STARCH

Pearl Corn Starch

Starch, as prepared by the wet-milling industry, is divided into many classifications and modifications of the parent starch. In general usage in the paper industry, the term "unmodified starch" denotes a starch with no further treatment other than normal refining, cleaning and drying. In the case of corn starch, this product generally has the appearance of a white, granular material and has a moisture content of 10 to 12 percent. This granular appearance has led to the term "pearl corn starch", and in general, this term describes an unmodified starch. This unmodified starch is the raw material from which all subsequent modifications and derivatives are made.

The wet-milling industry processes the corn in a manner designed to remove each constituent of the corn in a separate operation to arrive at the starch portion. Corn comes to the mill generally at 61 percent starch.

The corn is delivered, shelled at the plant and is unloaded through the primary corn cleaners to storage. It is then conveyed to the steep tanks and, if necessary, through a second cleaning operation on its way to the steeps. It is then held for approximately two days in warm sulphurous water at about 122°F. Upon leaving the steep, the corn is passed through stages of grinding and germ separation. This frees the germ so that it can be removed in a flotation process. The remaining components are

then passed to further refining equipment where the gluten and other fractions are recovered.

The starch is further washed and finally dried in air dryers, drum dryers or flash dryers under carefully controlled conditions. The end product of this treatment is the unmodified or pearl corn starch.

Converted Starches

Oxidized Starches

Oxidized starch is commercially produced from raw, unmodified starch in a two-fold reaction in which oxidation occurs predominately at the number two, three and six carbon atoms (19). The primary hydroxyl at the number six carbon and the secondary hydroxyls at the number two and three carbons are oxidized to carboxyl groups, using sodium or calcium hypochlorite as the normal oxidizing agent. Products of the reaction are carboxyl groups, which increase in number as the pH is increased; and aldehyde groups, found in greater numbers as the pH is decreased (3).

The other reaction which is carried out in the production of oxidized starch is one of hydrolysis, similar to that in which dilute sulphuric or hydrochloric acid is used to cleave the polymer chain at the 1, 4 and, to a lesser degree, at the 1, 6 glucosidic linkages (2). The extent of the hydrolytic reaction is governed by the desired degree of substitution and the desired viscosity of the cooked starch dispersion, e.g., the greater the degree of hydrolysis, the lower the viscosity.

However, there is a different reaction that takes place in the oxidation treatment, as compared with acid modification, that produces a different type product. In the oxidation treatment, some of the anhydroglucose units are opened up, and a carboxyl group is introduced into the polymer. This produces a product with desirable characteristics for paper applications. The resulting starch has increased water holding and water adsorbing qualities which decreases the tendency to penetrate the paper or migrate in a pigmented formula. The tendency to setback or retrograde is also markedly reduced, due to the introduction of the carboxyl groups which makes the polymer less linear with a consequent reduced tendency to reassociate. They also have improved film clarity and lower cooling temperatures, as compared with the unmodified parent starch.

Oxidized starch is used in the paper industry as a surface sizing agent and as a coating adhesive. The main purpose of a surface size is to impart fiber bonding at the surface of the paper web. Oxidized starch is often used instead of other surface sizing or coating agents because it has good strength imparting and flow properties and is economical. Through the repulping of surface-sized or coated broke, oxidized starch enters the wet end furnish in concentrations high enough to cause drastic decreases in filler retention and primary effluent settling rates. The efficiency of primary clarifiers is sharply decreased and coagulant costs are increased. The effluent from a primary clarifier operating under

these adverse conditions is highly turbid and often imparts a milky streak to the receiving water which is visible evidence of pollution.

Thermal-Chemical Starch

The Thermal-Chemical Conversion System for continuously pasting and modifying starch is a major technological advancement. This system makes it possible to use unmodified corn starch for the entire range of paper or board products that normally use a starch adhesive. The system converts unmodified starch into adhesives equal in performance, or superior to, those produced by enzyme converting starch, by cooking acid modified, oxidized, or ethylated starches, or from cationic starches.

There are many advantages to this process, for example lower starch costs, since the conversion process uses an unmodified starch which is the lowest cost and most available domestic starch. Another advantage is single starch inventory, since all that is needed is one starch so that now you can buy in bulk form. Lower starch consumption is generally seen due to the completely gelatinized and thinned nature of the starch. There is a significant savings in utilities due to high solids continuous cooking. Adhesive control is very easy. The degree of polymerization can be simply controlled by changing the chemical addition rate. Last, there is little change or setback of the size press adhesive when allowed to sit.

It is generally accepted that present thermal and thermal-chemical converting techniques, utilizing pressure cooking, pro-

duce a paste containing more of the desired components, macro-molecular starch bundles, and molecularly dispersed amylose and amylopectin, than do conventional batch cooking procedures at atmospheric pressures.

When the solids of an unmodified corn starch paste are increased, the paste becomes so viscous that it is difficult to use. With high temperature pasting under agitation, solutions of 3 to 4 percent solids may be utilized. To obtain even higher operating solids, some chemical modification must be employed or more mechanical energy must be used. The chemical modifier we are going to concern ourselves with is ammonium persulfate (AP), which reacts with the starch to achieve the desired viscosity reduction.

Viscosity reduction of a starch paste is a combination of physical dispersion of the starch, using heat and agitation, with an accompanying reduction in molecular chain length brought about by chemical reaction. The reaction may be considered to take place in three steps:

1. The oxidizing agent is converted to the active free radical form through the application of heat. This takes place concurrently with the initial stages of pasting the starch.
2. The free radical produces starch chain cleavage with formation of acidic groups.
3. The acidic groups cause additional chain cleavage.

The primary variables involved in the chemical reactions are temperature, time, pH and reactant concentration. Absolute control of these variables is essential in order to produce a predictably uniform adhesive. In addition to their effects on the chemical reaction, these variables also are the major factors which influence the physical dispersion of starch.

Thermal-chemical conversion of starch has been utilized with a wide variety of application systems:

1. Inclined, horizontal and vertical size press.
2. Gate roll size press.
3. Calender stack.

Thermal-chemically converted starch paste can be prepared to obtain a desired viscosity at any solids level used for size press application. The ability to independently control the starch solids and viscosity enables the papermaker to choose the exact converted starch paste property for each application. For consistently good quality paper, the desired combination of temperature, starch solids, and viscosity must be determined and precisely maintained.

High temperatures and pressures employed in thermal-chemical conversion produce a more highly dispersed paste that can be obtained with atmospheric systems. Thermal-chemically converted starch paste is more completely dispersed. It has greater binding ability when compared to starches prepared using the

atmospheric cooking systems. More costly premodified starch pastes generally have equal adhesive power when pasted at high temperature and pressure.

Ethylated Starches

A number of processes have been developed whereby starch in its native, ungelatinized granule form is etherfied to a low level of substitution, generally from 0.05 to 0.10 hydroxyethyl group per D-glucose unit, without significant granule swelling or degradation of the starch polymer chains.

The process most widely used by corn wet-milling companies in the United States is the wet-process reaction. Starch in a 40 to 45 percent solids suspension is made alkaline with an alkali metal hydroxide or alkaline earth metal hydroxide. Ethylene oxide is dissolved in the suspension.

The reaction is conducted at temperatures well below the swelling temperature of the starch, usually not exceeding 50°C. The introduction of hydroxyalkyl groups lowers the swelling temperature of the starch. Swelling of the starch to an unfilterable state can be prevented by the addition of swelling inhibitors such as neutral alkali metal salts. By using these salts, sufficient strong alkali can be added to starch suspensions to promote efficient and relatively rapid reaction with epoxy reagents. Degrees of substitution up to 0.1 hydroxyalkyl group per D-glucose unit are easily obtained in commercial production without loss of filterability.

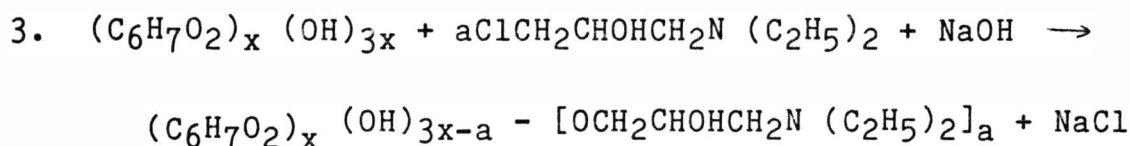
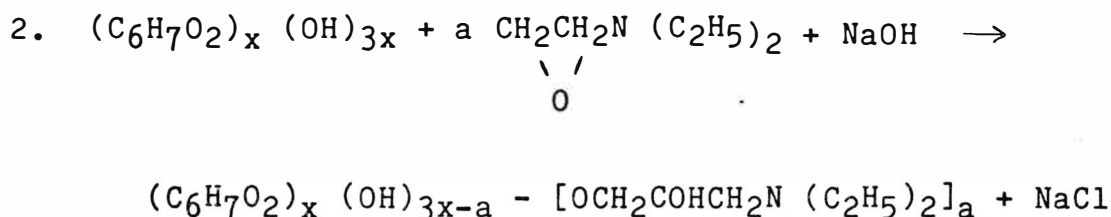
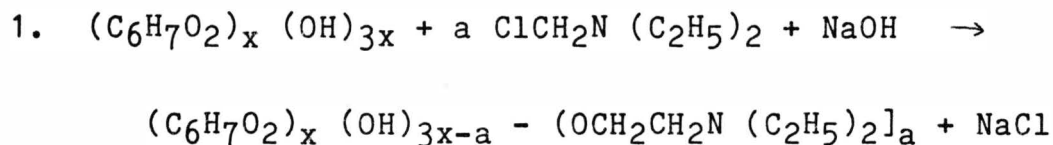
Generally, the introduction of hydroxyethyl group in starch results in a reduced gelatinization temperature, increased rate of granule swelling and dispersion on cooking, increased paste clarity and cohesiveness, and a greatly lowered tendency of pastes to gel and retrograde on cooling and aging. Film clarity, flexibility, smoothness and solubility are substantially improved. Ether linkages are not cleaved by acids, alkalis and mild oxidizing agents. Thus, hydroxyalkylated starch can be subjected to various depolymerizing treatments to obtain a wide range of viscosity grades without altering the substituent groups.

They are widely used at the tub, size press and calenders to improve sheet strength and stiffness as well as surface characteristics. The improved water holding properties and cohesiveness of starch hydroxyethyl ethers decrease the tendency of the wet films to penetrate into the paper, which results in a more continuous surface film. Films of hydroxyethyl starch shrink less on drying and, because of minimized retrogradation tendencies, are smoother, more continuous and more flexible than those of underivatized starch. The film continuity of hydroxyethyl starch is especially important because it increases the resistance of paper surfaces to penetration by hydrophobic materials such as grease, wax, varnish, lacquer and inks.

Cationic Starch

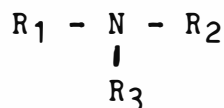
Patents

There are many ways to convert a pearl starch to a cationic starch; however, it is beyond the scope of this report to list all the methods. This report will concern itself with the cationic starches prepared from amines. There are three different methods: 1) reaction of starch with beta-halogenated amines in the presence of sodium hydroxide; 2) reaction of starch with glycidyl tertiary amines in the presence of sodium hydroxide; and 3) reaction of starch with 3-chloro - 2-hydroxypropyl tertiary amines. Following are the three reactions for these three methods:



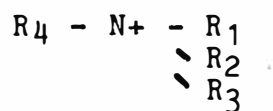
As was stated before, there are many ways to prepare a cationic starch, following is one of the methods: This method relates to the preparation of starch ethers containing quaternary ammonium substituents. In other words the starch is retained in the granule form during the etherification reaction and in which cross-linking is avoided or kept at a minimum (29).

Paschall (29) discovered that nitrogenous products of this nature may be prepared by reacting starch with the reaction product of epihalohydrin and a tertiary amine or a tertiary amine salt (e.g., a salt such as is obtained by treating a tertiary amine with hydrochloric acid or sulphuric). Tertiary amines suitable for his invention can be represented by the formula:



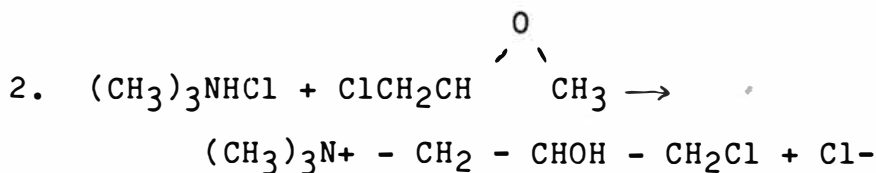
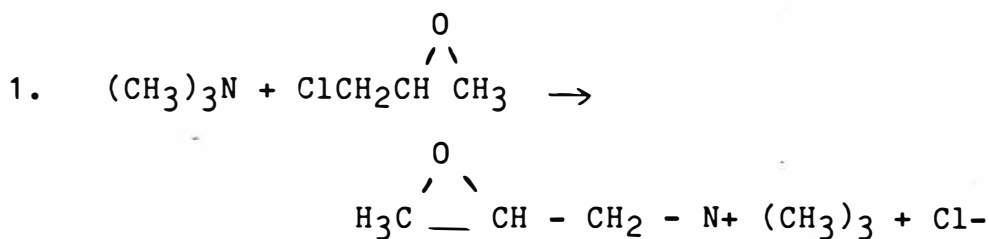
wherein R_1 , R_2 and R_3 are from the group consisting of alkyl, substituted alkyl, alkene, aryl, aralkyl, but if each are the same, they each should not contain more than four carbon atoms.

The reaction between epihalohydrin and the amine or amine salt results in compounds which may be represented by the formula:

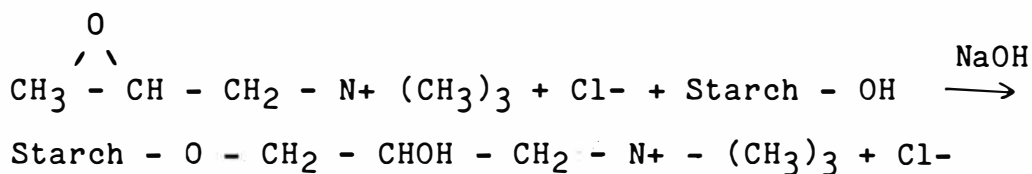


wherein R_4 is 2,3 epoxypropyl if the free amine is used, and R_4 is 3 halo 2 hydroxypropyl if a salt of the tertiary amine is used.

The reaction between the epihalohydrin and amine may be shown by the following equations, using trimethylamine and trimethylamine hydrochloride and epichlorohydrin for illustrative purposes.



The reaction of starch and the epihalohydrin reaction product may be illustrated by the following equations, wherein the reaction product of trimethylamine and epichlorohydrin is representative:



Following is the formulation of a granular quaternary ammonium starch ether from the trimethylamine hydrochloride reaction product, which was invented by Paschall (29).

A 30 percent aqueous solution of trimethylamine was added to 0.1 mole of NHCl in 100 ml of water until the pH was 8.5.

Epichlorohydrin (0.1 mole) was added and the mixture stirred at 30°C . for one hour. The aqueous solution was vacuum distilled to a solid white residue consisting of 3-chloro; 2-hydroxypropyl trimethylammonium chloride. The chlorohydrin was cyclized to the epoxide with 0.1 mole of NaOH in 100 ml of water.

A mixture consisting of 1 mole of starch, 0.14 mole of Na_2SO_4 and 0.06 mole of NaOH in 250 ml of water was added to the purified reagent. The slurry was then stirred 18 hours at 40°C . The reaction mixture was neutralized to pH 7.0 with HCl , filtered and the filter cake washed with water. The air dried product contained 0.41 percent nitrogen, equivalent to a degree of substitution of 0.05.

Theory of its Affect

Cationic starches represent a unique class of high performance starch derivatives which have recently gained commercial acceptance. Their industrial importance resides in their affinity toward negatively charged substrates such as cellulose and some synthetic fibers. They also appear to function as internal binders and retention aids for various fillers and emulsions, and sizing agents for natural and synthetic fibers. The reason that the cationic starch has a strong affinity for negatively charged substrates is that it is a positively charged starch molecule.

Because of the electrochemical attraction of the starch to the fiber, the cationic starch is able to give a stronger, more uniform surface to the paper when compared on an equal additive basis to non-cationic starches (4). Since this attraction does exist, the solids at the size press application may be reduced by as much as 50 percent in some cases, and is still able to maintain sheet strength (5).

It has been shown that less cationic starch is needed to maintain surface strength and quality. When cationic starch is applied to a sheet, it is immediately attracted to the negative charged fibers on the sheet's surface. As more starch is applied, it seals the sheet's surface and hinders any further starch penetration into the sheet. Some starch does penetrate, but only to a certain extent, while the majority remains on the surface of the sheet, forming a superior film.

The mechanism for cationic starch molecules hindering the penetration of the starch too far into the sheet is as follows: The cationic starch being electrochemically attracted to the fibers, will, when applied to the sheet, readily attach themselves to the fibers. Since the starch molecules are readily attached to the fibers, they do not have a chance to penetrate the sheet too far. So the starch molecules which initially enter the sheet are retained by the fibers near the surface, and physically hinder the penetration of the molecules following.

There are many advantages to using cationic starch over conventional starches at the size press. Since less starch is needed when cationic starch is used, an improvement in opacity should be seen, increased machine speed through easier drying after the size press, and the possibility of running lower viscosities at the size press for improved operability. However, one of the most important advantages over that of conventional starches is that it improves printing characteristics of the sheet.

A combination of the fiber bonding and surface orientation explains the improvements in printing properties. The fiber bonding provides a good strong surface while the uniform starch concentration on the surface makes for a uniform ink receptivity and good ink holdout (5).

Some of the improvements in printing by using cationic starch are as follows: (3) better print definition; better depth of color; less ink show-through to the back side of the sheet; and less "ghosting" in printed illustrations. The improved press operability was due to less dusting and fewer pickouts which led to longer press runs. Less milking in offset fountains also contributed to longer runs.

When a conventional starch is being used at the size press, a lot of it is needed to impart the desired strength properties to the sheet and is greater for lower basis weight sheets. If, however, the desired level of surface properties can be achieved with significantly lower pickups of starch, an equally significant increase in opacity will occur.

This in turn can mean a substantial reduction in the amount of TiO_2 or other high grade fillers generally required to achieve high opacity.

Another advantage, and probably a main one, is its ability to remain with the fiber, and hold fiber, fillers and coatings together during the repulping operation. This means that less soluble starch enters the mill effluent and thus can lead to significant reductions in mill effluent BOD.

SIZE PRESS

Purpose - Functional Coatings

A good definition of sizing is (7) a treatment applied to the paper surface to improve finish, produce a surface better suited to printing, minimize scuffing, control densometer, prevent excessive or undesirable penetration of other finishing agents, decorate or improve appearance and improve strength characteristics. Another source defined size as (8) any chemical, other than bleach, fillers, pigments and dyes which are added to the papermaking furnish or subsequently applied after the web is formed, which alter those characteristics of the sheet that relate to the transudation or absorption of liquids which come into contact with the web.

The purpose of the size press is to incorporate additives onto or into a sheet after formation, pressing and almost complete drying. Compared with furnish addition, surface treatments do the following (9) (11):

1. Allow higher levels of addition with relatively little loss of material.
2. Afford better control of location in or on the sheet.
3. Avoid such problems of wet-end addition as reduced drainage, plugged wires or wet felts, slime buildup and poor retention.

Along with all the advantages of using a size press follow several disadvantages, but minute when compared to the advantages. The disadvantages are (11): a) the rewetting of the sheet after drying, hence requiring extra drying and reduction in machine output; b) the capital costs involved with a size press installation; and c) preparation cost of starch whether by enzyme, oxidation, acid or heat.

Types of Size Presses

The size press is simply a pair of press rolls which may be arranged in three configurations. The oldest type is the vertical press (Figure 1) with the solution being showered on each roll where a pocket is formed by the downward sloping sheet and the top roll. The overflow flows into a pan underneath.

A problem with the vertical press is (9) the pond of solution on the top side of the sheet. The pond may deform the sheet if too heavy, resulting in unequal top to bottom side absorption.

The horizontal press (Figure 2) was designed to overcome the problems of the vertical press. The horizontal size press has the rolls placed in a horizontal arrangement. A spout in the center of the trough delivers an equalized pond of starch on each side of the sheet, the excess starch runs off each end of the press into small catch funnels. If it is desired to apply size to only one side of the sheet, (12) water is usually applied to the other side to counteract the moisture addition in the size.

Experience indicates (13) that it is possible to apply heavier coatings with the horizontal press because the depth of the pond in the vertical press is very small so that any tendency to force the size into the sheet is due purely to absorption and such velocity pressure as can be built up in the nip. The horizontal press has a nip which is completely submerged and also subjected to a hydrostatic head.

Then comes the inclined press (Figure 3) which has been developed to avoid the rather awkward vertical run of the sheet into the horizontal press.

The roll loading, diameter, crown and hardness are other variables of the size press equipment.

The higher the nip pressure (13) the less the amount of size pickup as the size is more effectively squeezed out, and the larger the roll, the more nip pressure must be applied in order to squeeze out the same amount of size.

The size press nip can be conveniently divided into three regions (10) as shown in Figure 4. As the paper enters the nip, it passes through a pond of sizing solution and absorption of liquid into the sheet takes place. It then passes through a region of shear where the sheet may be compressed and liquid may be forced into the sheet. On the exit side of the nip, hydrodynamic metering and film splitting take place, probably by a cavitation and filamentation mechanism.

The crowns are kept to a minimum and as the rubber covered roll is made softer, there will be a tendency (12) toward more size pickup due to the wider nip line which effectively reduces the contact pressures. Also the contact time varies directly with size pickup and penetration.

Theory of Pickup and Penetration

Pickup

There are two basic mechanisms which incorporate starch solutions into the sheet (9). The first is the ability of the sheet to absorb the fluid size. Practically all the absorption takes place between the first contact with the sheet and the point of maximum pressure in the nip. Following are a list of factors of absorption:

1. Machine speed, inversely, since there is less time for absorption at higher speeds.
2. Size viscosity or fluidity. The more fluid, the more rapidly the size soaks into the sheet. Fluidity depends upon the type of rheology of the size, concentration and temperature.
3. Moisture which has a direct effect. Very little size will absorb into an oven-dry sheet. As moisture increases, so will absorption. Practically, the most accepted moisture range is (14) 4 percent to 12 percent moisture entering the press.

4. Internal sizing inversely affects absorption. One investigator (15) reports that internal size levels below those detectable by ordinary size tests will limit absorption.
5. Sheet porosity or void volume will interrelate with nip pressure for the final amount absorbed in the nip itself.
6. Pond area - differing contact time for absorption between the top and bottom surfaces of the sheet.

The second mechanism affecting pickup is the amount of solution film passing through the nip, and the character of the split when roll and paper separate. This largely determines the amount of starch remaining near or on the sheet surface. Following are the factors affecting filming:

1. Most important is the hydraulic wedge pressure which is built up by the fluid entering the nip. This pressure acts to force the rolls apart and allow the film to pass through. This pressure increases with both speed and viscosity.
2. Sheet surface quality, with a rougher sheet carrying more size.
3. Both nip pressure-per-unit area and roll hardness act counter to the hydraulic wedge pressure, to express the starch from the nip. Roll diameter will define the nip pressure-per-unit area at a given lineal press loading.
4. Sheet leadout, degree of wrap and draw tensions will affect the film split and final film left on the sheet.

Machine speed has an effect on the pickup. One source (9) has absorption decreasing, but at a lessening rate, while the filming pickup increases linearly. While the other source (10) has pickup first decreasing and then an increase in pickup with increasing machine speed. The reason for this is that the absorption term is dominant at low speeds, leading to a decrease in pickup as speed is increased. But at the higher speeds the hydrodynamic term is more important and produces an increase in pickup with increasing speed.

Penetration

There have been many ideas concerning penetration. Two of them are as follows: 1) If penetration is good or bad - does it affect the future use of the sheet and what are the economics; 2) How to change the degree of penetration of the size. The theories regarding penetration can be divided into three groups. These are the machine, sheet and size solution variables.

When discussing the degree of penetration of a starch into a sheet, several factors must be considered (6). These factors include:

1. Degree of internal sizing.
2. Solids/viscosity of the applied starch.
3. Moisture of the sheet coming into the size press.
4. Density and porosity of the sheet.

5. Relative surface tensions of solid and liquid phases.

6. Size press variations such as:

- a. Nip pressure.
- b. Size of starch pond.
- c. Roll positions, draws, speeds.

The most general equation found on penetration of a liquid in a sheet is as follows (6):

$$l^2 = \frac{r \gamma \cos \theta t}{2 \mu}$$

Where: l = depth of liquid penetration in cm.

r = paper pore radius in cm.

γ = surface tension of liquid in dynes/cm.

$\cos \theta$ = cosine of angle taken by liquid in contact with solid.

t = time of penetration in sec.

μ = coefficient of viscosity in poises.

The above formula for theory of penetration can be used to estimate the depth of penetration.

Viscosity is the most important variable of the size solution.

The penetration, as seen by the above equation, is inversely proportional to the square root of the viscosity. The solids content is another important variable, and is related to viscosity.

The paper machine variables produce an effect by changing some of the previous variables mentioned. Therefore, increasing the

machine speed would decrease the dwell time and as previously stated, decrease the starch pickup and penetration. The temperature at the machine will probably have the effect of changing pickup and penetration. Previous pressing on the machine will effect the moisture content, density and sheet surface. Previous drying will affect the moisture content. The secondary variables affect the previous variables mentioned, and for the reasons given for the previous variables, affect the size penetration and size pickup.

By using starch either as the basic surface sizing agent or as a carrier for other types of additives, the papermaker is able to work over a wide range of cooked paste viscosity-solids relationships. Thus, applications may run from unmodified, high-viscosity products at low solids for a light surface treatment, to highly modified products which can be prepared over a wide range of viscosities to give a desired degree of penetration. As a rule, the higher the inherent viscosity of the starch, the stronger its adhesive qualities. For this reason, the starch of the highest possible inherent viscosity should be chosen for a given application, consistent with the viscosity limitations of the press and the particular results that are required.

Effects on Physical and Optical Strength

The size press is used for low solids, pigmented wash coatings for the improvement of surface characteristics or for precoat treatment. Such coatings improve surface smoothness and ink

receptivity, reduce sheet porosity and provide an overall better appearance. In general, surface applications may provide (9):

1. Improved internal strength as measured by mullen, tensile, internal bond or fold.
2. Improved surface properties as measured by wax pick, IGT, scuff resistance, smoothness, erasability or reduced linting.
3. Improved water, ink or grease resistance.
4. A vehicle for pigments of functional materials.

Investigators estimate that (9) normal paper sheets have 50 percent or better void volume. It follows that these voids cannot take up more than their own volume of wet size solution. On drying, this volume will shrink away, leaving the solids coating the fibers, but no longer filling the voids. Incorporation of a pigment, normally clay, will go far toward achieving a more closed sheet with a more continuous and smooth surface.

The one universal requirement for a successful size press coating is a level application free from visible patterning. On passing through the size press nip, the binder-pigment film is stretched and split as the roll and paper separate. The fluid is drawn out in fine stringlets which break and contract back onto either surface. Normally the droplets will reform back into a film; however, those applied to the surface of the sheet will set and solidify as streaks. Under the poorest of conditions the streaks will be visible to the naked eye. Under the best of conditions,

the patterning is still present but the streaks are too fine to be seen, and the coating has the appearance of a continuous coating.

Investigative work (9) on patterning has shown that a thixotropic binder of high viscosity (within limits of the size press capabilities) is necessary. The viscosity of such a coating is minimum at the point of high shear in the nip, resulting in a cleaner split with finer stringlets. Various derivatized starches not only have these desired properties, but also provide the necessary adhesive strength to bind the pigment to the surface.

ENVIRONMENTAL CONCERNS ASSOCIATED WITH STARCH

Of major concern to the paper industry is the environmental impact of residual or "secondary" additives in furnishes containing recycled fibers. These additives, depending on their ionic nature, can have a variety of detrimental effects on performance characteristics of primary additives, paper properties, fillers and fine retentions, and consequently mill effluents. Conventional surface sizes, because of their "nonionic" nature and levels of addition, are prime offenders in the recycled furnishes. They are not strongly attached to the fibers, and unless systems are specifically tailored for their presence, they are discharged in mill effluents. In addition to increasing the suspended solids and BOD of the effluents, the residual additives, because of their dispersive action, can often seriously affect clarifying processes.

One of the biggest problems starch contributes to the environmental problem is it adds to the turbidity problem in mill waste water effluent. (5) With the emphasis on broke and secondary fiber usage, this problem has grown. The primary adverse effect of starch-bearing broke or secondary fiber results from the repulping of this material. In the repulping operation the starch is dissolved, thus releasing pigment and fiber fines from the rest of the fiber. As this material is reintroduced to the system, much of it is lost through the machine wire and saveall system and discharged as mill effluent. This turbidity contains fiber, filler and chemical additives which the papermaker sees as

higher production cost when lost to the receiving streams.

Today, the aim is for reusable water which must be obtained economically by treatment of white water. If the white water turbidity cannot be removed, it must be ultimately discharged to the receiving stream. The starch-turbidity problem is increased three-fold: 1) The fresh water use is increased, 2) the volume of waste water to be treated is increased, and 3) a more difficulty treated effluent is produced. (3)

Another problem not to be overlooked is the biological oxygen demand, (BOD) of the starch component of the waste effluent. It has been shown that starch can exert from 0.5 to 0.75 pounds of BOD per pound of starch used. (16)

It is then highly favorable to have the starch remain with the filler and fiber to be removed at the savealls to be reintroduced to the paper furnish and eliminated from mill waste water returning to the receiving stream.

The anionic starches have showed many of these problems stated above. Because of this reason the papermaker is in search of a new starch or chemical substitute for a sizing agent. The cationic starches have been found to partially solve the problem of stream pollution. It has been observed that cationic starches can greatly reduce effluent BOD. (17) The size press can be a major contributor to BOD of the mill effluent. Because of cationic starch's high electrochemical attachment to the fiber, it isn't removed during the repulping cycle where much of conventional starch is lost to the sewer.

Cationic starches are currently being used in increasing amounts for size press applications in an attempt to minimize or obviate the negative effects of residual additives.

Seven sizing materials, including anionic, cationic, and nonionic products were evaluated in a study (18). The cationic efficiency of the experimental derivatives were measured, and the cationic efficiency was higher than that of the commercial cationic size. Strength increases resulting from the residual sizing materials in the recycled papers were evident in all trials, especially in those with concurrent increases in filler retention.

It was found in this experiment that there is advantages of using the higher cationic efficiency sizes, when the sized paper was introduced as broke in a secondary fiber system. Residual size retention in these systems, and its effect on sheet strength and filler retention, were directly related to the cationic efficiency of the surface-sizing material. Effects of the residual sizes on suspended solids and COD of the effluents could not be clearly established.

EXPERIMENTAL

Introduction

The main objective of the laboratory procedure and testing was to compare the five different starches at three solids levels for their optical, physical and BOD results when applied at the size press. The question to be answered here is, is the starch you are using really worth the money you are paying for it, or can you use a cheaper starch and still get the same properties.

Problems

A big problem with trying to run an experiment like this is that there are many variables involved. One of these variables is that the starch properties change when under shear at the nip. So to categorize the starches, the alkali dudley viscosity method was used. This method could possibly pin point the molecular weight of the starch. Also to help this problem out, the starches were ran at three solids level, this categorized them also. Another problem was how to measure consumption of starch at the size press. Appendix 2 will explain this, and Appendix 1 will explain the alkali dudley viscosity method.

Machine Run

The ethylated, oxidized and cationic starches were made up the night before, and the thermal-chemical starch was obtained from a local paper company in the morning. The thermal-chemical cationic was made using the on-site cationization process. The paper to

be sized was made up ahead of time, and was hooked up between the large dryer section and the press section on the pilot fourdrinier.

A couple of the dryer cans were heated up in the large dryer section to heat the paper up to normal running conditions. The paper was then ran through the size press, then dried between 190 - 210°F., and without any pressure on the calender stacks. Table 1 shows the machine run data results and is self-explanatory.

With the machine running at approximately 90.0 fpm, the samples were allowed to run for about 6 or 7 minutes, when a uniform application had been achieved. The samples for testing were then randomly picked out of the center of the slabbed portions.

MACHINE RUN DATA
TABLE 1

Sample	Starch Solids	Brooksfield Viscosity	Dudley Viscosity	Starch Temp.	Sheet Temp.	PLI Nip Loading	Dryer Temp.	Machine Speed	Consumption
E-15	15.3%	540 cp	145 sec.	130°F.	190°F.	85	190-210°F.	91.6 ft/min.	----
O-15	14.8	30	47	130	190	85	190-210	90.2	563 lbs./ton
C-15	14.9	17,200	3,506	130	190	85	190-210	88.0	----
TC-15	11.9	3,400	585	130	190	85	190-210	87.8	----
TCC-15	12.5	220	204	130	190	85	190-210	86.6	----
E-11	11.4	22 cp	86 sec.	130	190	85	190-210	91.1	----
O-11	11.4	6	38	130	190	85	190-210	90.4	434 lbs./ton
C-11	11.8	780	159	130	190	85	190-210	88.8	----
TC-11	8.6	7	41	130	190	85	190-210	85.6	----
TCC-11	9.3	50	46	130	190	85	190-210	85.3	----
E-7	6.1	6 cp	39	130	190	85	190-210	90.7	265 lbs./ton
O-7	7.5	3 cp	34	130	190	85	190-210	90.1	326 lbs./ton
C-7	6.6	6	32	130	190	85	190-210	89.0	251 lbs./ton
TC-7	5.8	3	38	130	190	85	190-210	86.3	252 lbs./ton
TCC-7	6.5	15	36	130	190	85	190-210	84.5	283 lbs./ton

TESTING RESULTS

The following abbreviations will be used throughout the remainder of this paper:

E-15	Ethylated Starch at 15% solids
E-11	Ethylated Starch at 11% solids
E-7	Ethylated Starch at 7% solids
O-15	Oxidized Starch at 15% solids
O-11	Oxidized Starch at 11% solids
O-7	Oxidized Starch at 7% solids
C-15	Cationic Starch at 15% solids
C-11	Cationic Starch at 11% solids
C-7	Cationic Starch at 7% solids
TC-15	Thermal-Chemical Starch at 15% solids
TC-11	Thermal-Chemical Starch at 11% solids
TC-7	Thermal-Chemical Starch at 7% solids
TCC-15	Thermal-Chemical Cationic at 15% solids
TCC-11	Thermal-Chemical Cationic at 11% solids
TCC-7	Thermal-Chemical Cationic at 7% solids

Following are general conclusions of all the starches at all the levels, the final conclusions will be drawn on the 7 percent solids level.

Brightness

The brightness was not affected much by the different starches, and different solids levels. Most of the values did not deviate more than 1 percent from the value of the base stock. The worst

performer if you could call it that was the C-15, it was 1.2 percent lower than the base stock. The best starch was the TC-7, it was .3 percent higher than the base stock. Anything higher than the base stock should be significant, since you would expect starch to decrease brightness. The brightness in the TCC-7 was lower than the base stock, but this can probably be attributed to the fact that the opacity was higher.

Opacity

The opacity results deviated more than 1 percent on the other hand, most of the lower values were seen at the higher solids levels. The reason for the lower opacity could possibly be that too much starch was being added. As more starch is applied to a sheet, the opacity generally decreases. High solids and high viscosity will hinder penetration into the sheet. The base stock had an opacity of 87.2 percent. The worst opacity value was obtained from the E-15, with a value of 85.4. The TCC-7 obtained the best value, 88.5. This goes along with the literature search, in that a cationic starch will penetrate a sheet only so far, and then it will seal off the surface of the sheet. In this case less starch is needed so opacity should increase.

Tensile

The results from the tensile test were very satisfying. The values ranged from 18.9 for TCC-15 to 13.7 for E-7. The base stock had a tensile value of 12.6. If a cationic starch is performing right, it should give the sheet added strength, and in this case it was. The homemade cationic (TCC) and the cationic already made up (C) both performed well. In the 7 percent solids

category both the cationics had the highest values. An idea as to what gives the added strength to the sheet could be due to the fact that the starch has a stronger affinity for the fibers and fillers and will then tend to hold the sheet together better. The other starches do not have a strong affinity for the fibers and fillers, and so the sheet will be more easily broken apart.

IGT Pick

In running the pick tests the #4 ink was chosen, and for the most part 3 m/s was the maximum speed used. At the higher solids levels the oxidized starch had the highest value, this can probably be attributed to the fact that an oxidized starch is fairly strong, and also has a low viscosity at high solids levels, which would allow the starch to penetrate the sheet a little more and secure the surface. Again, in the other two solids categories the cationics came out on top again, with the TCC being the best. The same reasoning holds true here also, in that the cationic starch holds fibers together better and makes for a very strong surface to print on.

In looking the results over it looks like there is a point where you can add too much starch. The 15 percent solids values are lower than the 11 percent solids, but are pretty much the same as the 7 percent solids. In other words you can get the same pick values at 7 percent solids, as you can get at 15 percent solids. It looks like the optimum category is the 11 percent solids, however, the two highest values 195 and 192.3 are 8.6 percent

solids and 9.3 percent solids, respectively. So it seems somewhere between 11 percent and 7 percent solids there is an optimum solids level where great efficiency can result.

Hercules Size

The Hercules size test was run at 80 percent reflectance, for the use of determining the sizing efficiency of each starch. These results are more scattered, it seems that every solids level has a different starch as the best of the group. In the 15 percent category the oxidized starch has the highest value, but not far behind are the cationics. This can probably be attributed to the fact that with an oxidized starch more starch is being applied to the sheet. In the 11 percent category the ethylated starch has the highest value with the TCC having the lowest, this can also be explained like the above. Also the TCC in this category is not really 11 percent solids, but only 9.3 percent. In the 7 percent solids category the cationic has the best value, with the TCC close behind. This shows that at lower solids levels, the cationics are very efficient, and that enough starch will be picked up by the sheet to have it sized properly.

BOD

Because of their cationic nature, the cationic starches are supposed to be superior to their counterparts, the oxidized and ethylated starches. The reason for their superiority is their affinity for the cellulose fiber. The BOD results hold true to this claim.

When paper is repulped, the starch breaks away from the fiber and ends up in the white water system, and thus an increase in BOD is noticed. But with the cationic the starch stays with the fibers when repulped and is put back into the sheet.

BOD₅ was ran on all the starch samples, and some very satisfying results obtained. The high BOD results were from the oxidized and ethylated starches. The best results were obtained from the cationic starches, where some very low BOD values were obtained.

TEST RESULTS
TABLE 2

Sample	Coat Weight (g/m2)	Brightness (%)	Opacity (%)	Smoothness	80% Hercules Size (sec.)	Tensile (lb./15 mm.)	IGT Pick #ink/speed (cm/s)	Mullen (lb./si)	BOD 3 ml Sample (ppm)	BOD 5 ml Sample (ppm)
E-15	4.0	87.4	85.4	172	105.6	18.0	115.7	16.6	556	490
O-15	4.64	88.4	87.7	167	121.0	17.2	183.3	17.0	613	473
C-15	4.77	87.1	86.1	167	71.3	16.9	109.7	16.6	468	293
TC-15	3.75	87.3	86.3	173	104.4	16.5	148.3	15.7	552	460
TCC-15	3.71	86.4	87.0	158	102.3	18.9	123.3	17.7	132	121
E-11	3.03	87.7	86.3	168	128.9	15.1	165.0	16.2	767	484
O-11	2.70	88.1	87.3	162	103.9	14.9	131.7	14.0	488	455
C-11	2.84	87.7	86.9	162	106.4	16.9	150.0	15.5	122	91
TC-11	2.33	88.4	86.5	157	118.8	17.9	195.0	15.0	407	334
TCC-11	3.21	86.8	87.3	142	86.1	16.9	192.3	16.0	282	181
E-7	1.14	87.6	86.9	164	94.8	13.4	133.4	12.0	442	277
O-7	1.12	88.2	88.0	160	84.1	14.0	112.7	12.8	326	262
C-7	2.45	87.9	87.5	173	105.3	15.2	138.3	12.6	425	234
TC-7	2.17	88.6	87.5	160	91.7	14.4	138.3	12.2	322	325
TCC-7	1.81	87.8	88.5	154	91.1	16.8	146.3	14.2	72	61
Base Stock		88.3	87.2	200	68.7	12.6	31.7	10.5		

FINAL CONCLUSIONS

The above conclusions were general ones, just taking all the data and trying to compare it to each other. To draw final conclusions the 7 percent category was chosen since the solids levels were fairly close, the alkali dudleys were close, and the consumption rates were close. Another good reason for choosing the 7 percent solids category is that most size presses are ran at approximately this solids level.

The TCC-7 seems to be superior over all the other starches at this level. It had the highest opacity, best smoothness, tensile strength, IGT pick, mullen, and most significant of all, it had the lowest BOD results. In several of the tests where the TCC-7 did not achieve the best results, the C-7 on the other hand did. The ethylated and oxidized had low strength results and high BOD results.

SUGGESTIONS FOR FURTHER STUDIES

A couple of studies are suggested by the results of this work. One would be to run the trials again and look at the energy consumption needed to dry the sheet. A second study would be to use the coated sheets and see how much energy it takes to calender the sheet to the desired gloss.

APPENDIX 1

Alkali Dudley Viscosity

1. 55 grams D.S. starch paste.

Example: $\frac{55}{\% \text{ solids}} = \text{grams of starch paste}$

2. Add 55 ml 10% NaOH.

3. Mix well.

4. Bring to 500 g. total with Hot H₂O.

5. Put in water bath at 100°F.

6. Let stand one hour.

7. Run Dudley using standardized Dudley pipette.

APPENDIX 2

BOD₅

1. Approximately 10 g. of sample taken.
2. Add 500 ml of distilled water.
3. Put mixture into Waring Blender.
4. Repulp on high speed for 5 minutes.
5. Filter pulp through a Buchner funnel.
6. Save filtrate for the BOD test.

The BODs were run using the standard 300 ml bottles at varying dilution ratios.

APPENDIX 3

Consumption Determination

$$\frac{1"/\text{min.} \times (\text{Draw-Down}) \times 5004 \times \% \text{ solids}}{\text{Production Rate}} = \text{lbs./ton dry pickup}$$

Production Rate for run: 115 lbs./hr.

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